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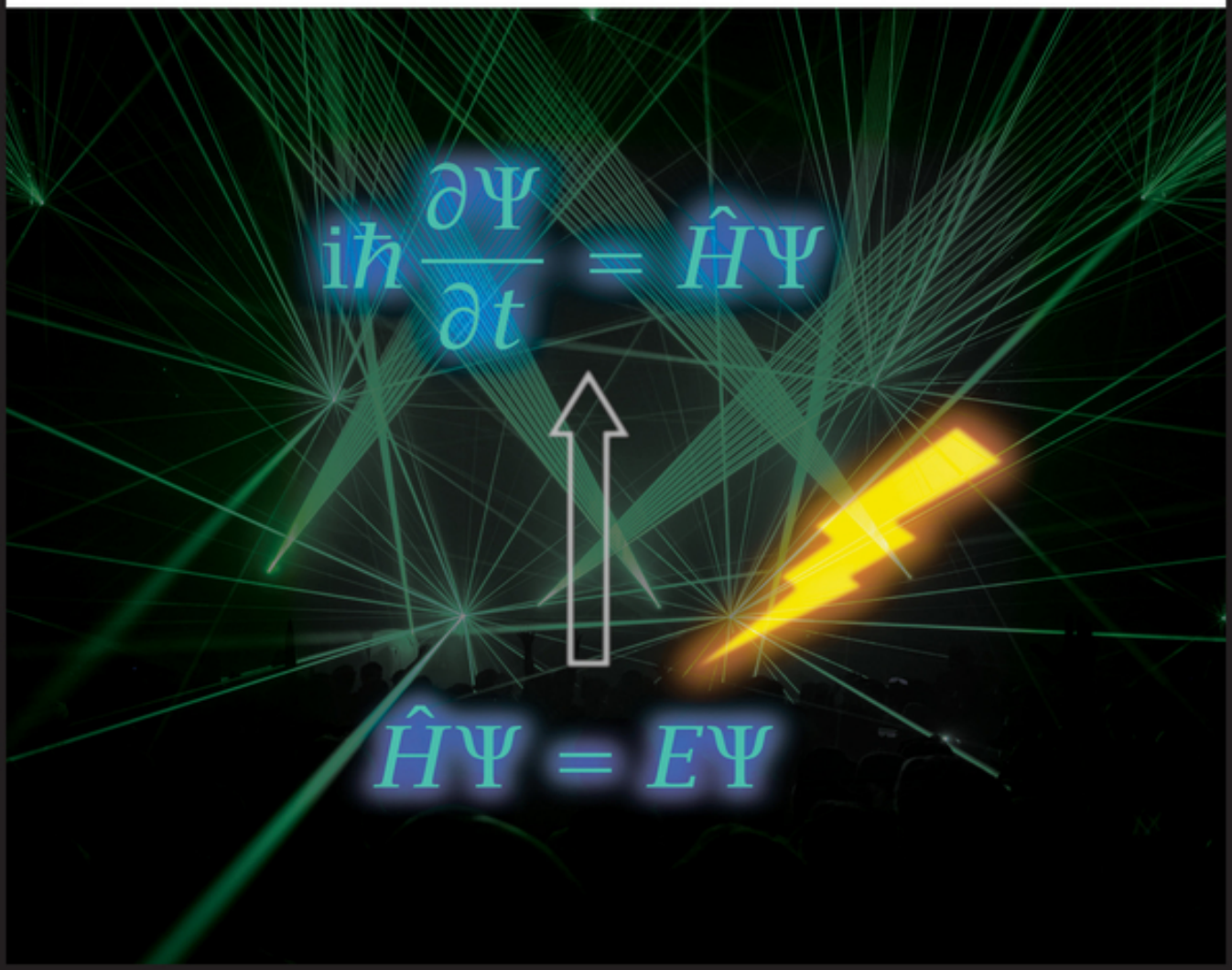
Leticia González and Roland Lindh

Quantum Chemistry and Dynamics of Excited States

Methods and Applications



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To our families,
for their unconditional love and endless support.

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Preface

Light is not everything, but without light there would not be life as we know it. For good reasons, the sun has been venerated in most ancient civilizations as a god. It has a powerful light and affects our lives on a daily basis. Light drives, controls, or is generated in numerous chemical reactions in nature. It is responsible for processes as essential as vision or photosynthesis, is part of the enchanting phenomena which is bioluminescence but can also be detrimental, such as causing skin damage. Its power has been exploited by mankind since earliest times, not only to heat but to heal, e.g., treating epidermal conditions, to name just one example. Today, sunlight is the hope for providing clean renewable energies. The ways in which the benefits of light can be harnessed go beyond the boundaries of chemistry, into physics, biology and medicine.

Driven by curiosity and interest, many researchers have been fascinated in understanding how light interacts with molecules as only then light can be rationally exploited in many applications. Theory is particular useful for this endeavor, as it allows many details, which are often invisible in experiments, to be disentangled. This particular research field, that could be termed as theoretical photochemistry, took off in the early nineties. Thus, the field is not new but there is still much room for further developments. When a molecule receives a photon of light, its energy changes, or in the language of quantum mechanics, it gets electronically excited. Thus, the computational study of electronic excited states requires the inclusion of quantum effects (at least in part) and this makes it still a challenging problem today except for the smallest molecules. However, recent years have witnessed an explosion of methods able to tackle the study of electronic states and its evolution in time in many different ways. This expansion has been accompanied by thousands of publications dealing with applications involving light. As of 2020, a search in the Web of Science with the words “excited states” and “theory” returned almost 30 000 hits, of which half are just from the last ten years! It is for this reason, that we considered it appropriate to bring this book to light(!), introducing advanced undergraduates, graduate students, and interested researchers to the many flavors in which the field has developed so far.

The book was born with the ambition to collect most of the computational methods that exist today able to solve first the time-independent and then the time-dependent Schrödinger equation for electronic excited states. Accordingly, after an introductory chapter dealing with basic concepts, the book is divided into two parts. Part I contains 9 chapters dealing with electronic structure theory, i.e., solving the time-independent Schrödinger equation and creating building blocks to be used in subsequent dynamics simulations. Part II is divided in 10 chapters devoted to the dynamics of molecules, i.e., solving the time-dependent equation. The solution to the former equation provides energies and other properties, of the electronic excited states in a static manner. It provides multidimensional potential energy surfaces and the corresponding wave functions associated to a particular geometry, which allow molecular spectroscopical properties to be computed. The latter

equation delivers a complementary picture of the system, being in motion, indulging time scales and predicting branching ratios. The richness and broadness of the book invites the reader to reflect on which method could be suitable for a particular problem. We hope that this book fills a gap in the theoretical and computational community dealing with light–matter interactions and becomes a guide in hand, as well as a reference for scientists in the field.

From basic theoretical foundations to the latest theoretical developments, every chapter is self-contained and encompasses the fundamental ideas behind a particular method, its strengths and limitations, as well as selected applications. The chapters are written with the aim to be understandable by master students and newcomers to the field while also informing experts about the state-of-the-art in the field.

Last but not least, we want to express our warm gratitude to all the authors who gracefully accepted the invitation to be part of this adventure, for their enthusiasm, patience and critical suggestions. We are also thankful to our coworkers, for lively discussions and helpful exchanges, in particular, to Philipp Marquetand, Sebastian Mai, Sandra Gómez, and Ignacio Fernández Galván. Their help was priceless.

Leticia González (Vienna)
Roland Lindh (Uppsala)

1

Motivation and Basic Concepts

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Abstract

This chapter describes what electronic excited states are and why they are important to study and therefore motivates the need for theoretical tools able to characterize them. Further and most importantly, in this introductory chapter, we put together in a comprehensive manner a collection of basic concepts that might be needed, depending on the background of the reader, to understand the remaining chapters of this book.

1.1 Mission and Motivation

When a photon of light strikes a molecule, the latter's electrons are promoted from the electronic ground state to higher electronic levels. Typically, the electronic ground state of a molecule is a singlet state, but depending on the number of electrons and their most favorable way of pairing, it can be a doublet, a triplet, or a state of higher multiplicity. Assuming the electronic ground state is a singlet, upon light absorption the molecule will be excited to another singlet state, as high in energy as the energy contained in the photon allows. Once excited, a number of radiative and non-radiative decay processes are possible. These are collected in the Jabłoński diagram shown in Figure 1.1(a), which assumes an electronic singlet ground state.

Radiative processes include fluorescence or phosphorescence, depending on whether the emission of light involves a transition between two states of the same multiplicity, for example from the lowest singlet S_1 to the S_0, or involves a change of spin, as shown in Figure 1.1, from the triplet T_1 to the S_0. Typically, as in the example depicted, the emitted light has a longer wavelength than the absorbed radiation because luminescence occurs from lower energy levels, and thus absorption and emission spectra are easy to identify from experimental data. In this example, the molecule returns to the original ground state from where it started and thus there was no photochemical reaction, one would say that a photophysical process has taken place.

Non-radiative processes can be much more complicated to observe experimentally, as they typically involve not only the bright or absorbing state defined by the wavelength employed to irradiate, but also dark states, i.e., states that do not have a significant oscillator strength but are populated from the bright states. A transition between electronic states of the same multiplicity is known as

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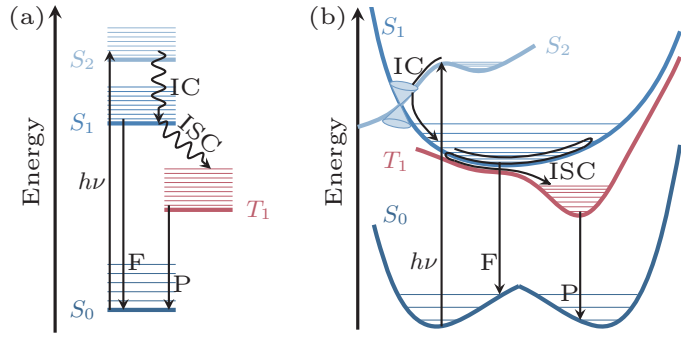

Figure 1.1 (a) Jabłoński diagram with levels. After absorption of a photon with energy $h\nu$, different processes can occur: radiative processes are fluorescence (F) and phosphorescence (P), non-radiative processes are internal conversion (IC) and intersystem crossing (ISC). (b) Jabłoński diagram with potential energy surfaces.

internal conversion, e.g., from S_2 to S_1. When two states of different multiplicities are involved, e.g., from the S_1 to T_1, one speaks of intersystem crossing.

The electronic levels of a molecule are defined through potential energy surfaces (PES) that extend along $3N - 6$ dimensions (with N the number of atoms contained in the molecule). PES are the direct consequence of invoking the Born–Oppenheimer approximation (BOA), see section 1.7. As comfortable as it might seem for a chemist to employ electronic states to envision the course of a chemical reaction from a reactant to a product, sticking to the BOA when talking about electronic excited states implies that the coupling between different PES is neglected. However, these so-called *non-adiabatic couplings* between PES are the "salt and pepper" of photochemistry, as they are essential to understand which states and geometrical conformations are populated after excitation. One key concept in this respect is the non-adiabatic transition around a *conical intersection*, see section 1.9. Named after the ideal topology two PES adopt when they intersect (see Figure 1.1(b)), a conical intersection is the molecular funnel that allows for internal conversion, and it can also be seen as the transition state in photochemistry, which connects a reactant with a product. Likewise, intersystem crossing is mediated by spin–orbit coupling, which is another form of vibronic or non-adiabatic coupling between electronic levels.

Figure 1.1(b) summarizes the radiative and non-radiative processes described before, now in terms of PES. If after the detour via the different PES, the molecule ends up at a different geometrical configuration from which it started after irradiation, one speaks of a photochemical reaction; if instead, it returns back to the electronic ground state of the reactant, the term photophysics is employed.

Be it photophysics or photochemistry, light-induced processes are all around us. As Ciamician already recognized in 1912[1], "reactions caused by light are so many, that it should not be difficult to find some of practical value". Indeed, just to give one representative example, the dream of using solar fuel to produce sustainable energy is keeping many scientists around the world busy. In an effort to mimic natural photosynthesis, one needs among others, to design efficient antenna complexes able to harvest the broad solar spectrum and direct the electrons towards the catalytic centers. This design requires a profound understanding of the underlying processes that take place in the molecules after light excitation. Theoretical modeling can help explain existing experiments and hopefully guide new ones. Which are the electronic states that are populated after

1 Giacomo Ciamician, "The photochemistry of the future", *Science* 36 (1912) 385–394.

excitation? How does the molecule evolve along the complicated PES associated to these electronic states? Often these two simple questions are not easy to answer. They imply a need to get an accurate solution of two key equations, the electronic time-independent Schrödinger equation and the time-dependent Schrödinger equation. Both equations are challenging to solve, except for very small molecules, and so approximations and numerical strategies are required. The solution of the first equation is the goal of electronic structure theory and the solution of the second, the target of chemical dynamics. Both fields have tremendously evolved in the last decades, with the emergence of many different methods that have a common objective.

The mission of this book is to keep up-to-date with the recent development in these two intertwined fields, setting the focus at solving electronic excited states and following their time evolution. Accordingly, Part I collects the most important electronic structure methods that can be used nowadays to calculate electronic excited states as well as associated PES and other electronic properties. Part II, in turn, covers the state of the art for solving molecular motion in the electronic excited states. The variety and extension of the methods collected in this book speaks for itself about how much progress has been achieved in this branch of theoretical chemistry, which undoubtedly has also massively profited in the last years from enormous advances in computational resources. It would not be fair, however, to pretend that theoretical photochemistry has reached its cusp. A deeper reading of the chapters will reveal to the reader not only how far we have come but also how much still remains to be done.

In an effort to make the contents of this book accessible to undergraduates and newcomers to the field, the rest of this chapter contains a number of basic concepts to ease the reading. All the chapters have been written in a fully consistent manner, so as to allow them to be studied independently from the others. The chapters are, nevertheless, organized such that they try to reflect a natural progression. In this respect, the chapters are grouped in two sections consisting of Part I and Part II – electronic structure theory and methods for molecular dynamics, respectively.

In the electronic structure section the selected order of the chapters tries, to some extent, to be in the order of sophistication. However, in some cases chapters are clustered together because of common grounds or methodology. In that sense, Part I starts with the chapters based on density functional theory (DFT) – the chapters on time-dependent DFT (TD-DFT) and multi-configurational DFT (MC-DFT). This is followed by chapters revolving around equation-of-motion coupled cluster theory (EOM-CC) and the algebraic-diagrammatic construction (ADC) scheme for the polarization propagator, which are grouped together due to the technical similarities of the methods. Finally, five chapters are grouped together based on the use of a configurational interaction (CI) type of wave function. Initially, the basics of the so-called complete active space SCF (CASSCF) and related methods – the foundation of multi-configurational quantum chemistry – is introduced. This is followed by two chapters on techniques describing how to solve the associated equations – the chapters on density matrix renormalization group (DMRG) and the quantum Monte-Carlo (QMC) approaches. To conclude Part I, two chapters about the inclusion of electronic dynamical correlation follow – the chapters on the multi-reference configuration interaction (MRCI) method and the multi-configurational reference perturbation theory (MRPT). A pictorial summary of the methods described is provided in Figure 1.2. Starting from Hartree–Fock (HF), different methods cover different degrees of dynamic and static correlation, all the way to the exact full-CI (FCI).

Part II, dealing with the time evolution of nuclear configurations, starts with three chapters that can be considered within the realm of quantum dynamics. The first one introduces the time-dependent Schrödinger equation and how to solve it exactly in a grid – what is known as wave packet dynamics. Due to the cost of obtaining PES, wave packet dynamics is typically done in reduced dimensionality. The multi-configuration time-dependent Hartree (MCTDH) family of

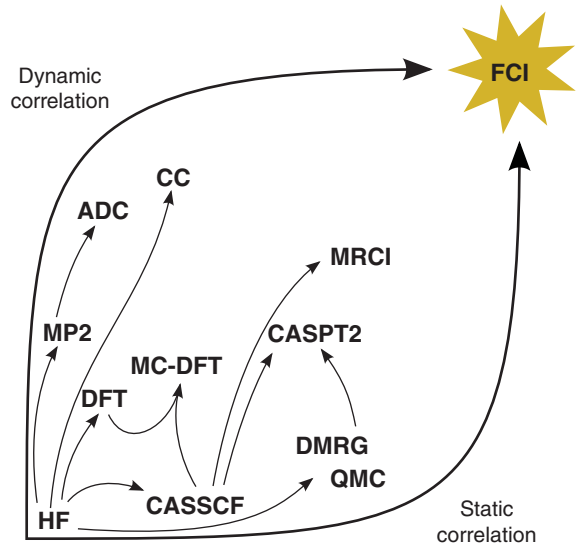

Figure 1.2 Scheme of quantum chemical methods for electronic structure. The lower left corner contains the most basic *ab initio* method, Hartree–Fock (HF), while the exact solution of the time-independent Schrödinger equation, full configuration interaction (FCI), lies, mostly unreachable, on the upper right corner. A panoply of methods described in Part I of this book, identified by their acronyms, try to "correct" HF, adding the missing *electronic correlation* and thus approximating the ideal FCI. The methods are arranged, qualitatively, based on their algorithmic relations and their prioritization of so-called *static* or *dynamic* correlation, which ultimately lead to the same end point.

methods is presented next, as a method that can alleviate in part the cost of grid-based wave packet methodologies. This chapter ends, bridging with the next block of four chapters that are based on quantum-mechanical and quantum-classical methods using on-the-fly computation of PES. These chapters are arranged in sort of going from more to less "quantum" – direct dynamics variational multi-configurational Gaussian (DD-vMCG) method, full and ab initio multiple spawning (FMS and AIMS), Ehrenfest methods, and surface hopping (SH). The next four chapters are based on alternative formulations of quantum dynamics. Exact factorization is based on an alternative way to express the electronic–nuclear wave function, Bohmian dynamics is based on wave theory, while semi-classical and path integral methods are based on Feynman's path integral formulation. Figure 1.3 illustrates pictorically the dynamical methods explained here.

Given the diversity of methods and authors it is unavoidable that every chapter follows its own writing style. For that reason, we considered it useful to collect here some underlying mathematical background, assuming basic knowledge of quantum mechanics, as well as a few photochemical concepts, that naturally arise in many chapters.

1.2 Atomic Units

A comment on atomic units is in order here. Hartree atomic units can elegantly simplify equations by setting to 1 the numerical value of some fundamental constants. Typical examples are the mass of the electron m_e, the electron charge e, the Coulomb or electric force constant $k_e = \frac{1}{4\pi\epsilon_0}$ and the reduced Plank constant $\hbar = \frac{h}{2\pi}$. Other useful constants used as units, derived from those fundamental quantities and used in this book are the bohr, $a_0 \approx 0.529$ Å, and the hartree, $E_h \approx 27.21$ eV.